

CONTROL AREA IN THE MANUFACTURE OF DIKETENE

DIKETENE

A NEW INDUSTRIAL CHEMICAL

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\OMPARED to the majority of aliphatic chemicals introduced to industry in recent years, the ketene dimer, or "diketene", which is now available in commercial quantities, is a comparatively new compound; it was discovered just thirty years ago. In 1907 the parent substance, monomeric ketene (CH₂=C=O) was first prepared by Wilsmore (51), who obtained it by immersing a glowing platinum wire in liquid acetic anhydride. Somewhat later Staudinger described its preparation by reacting bromoacetyl bromide with zinc (48). The great tendency of ketene to polymerize was soon observed by these investigators, and in 1908 Chick and Wilsmore first isolated diketene from the products obtained by allowing ketene to polymerize in sealed glass tubes (14). A more detailed description of the preparation and properties of this compound was published in 1910 by the same authors (15), who stated in their paper that "the preparation of cyclobutane-1.3-dione (diketene) may be recommended as a useful exercise for students in laboratories where a supply of liquid air is available". Hence, because of the obvious difficulties encountered in preparing adequate quantities of diketene, even on a laboratory scale for experimental purposes, it is not surprising that so little work has since been done on it. Now that a process has been developed for its commercial production, we may reasonably assume increased academic and industrial interest in the chemistry and uses of diketene and its derivatives.

Four structural formulas have at various times been proposed for diketene:

H_2C —CO	CH ₃ COCH=C=O	CH3-C=CH	$CH_2 = C - CH_2$
$UU = U \pi_2$		0-00	0-00
T	T	III	IV

Formula I, cyclobutane-1,3-dione, proposed by Chick and Wilsmore (15), from a consideration of both the physical and chemical properties of diketene, has been found to be untenable (33). Formula II, acetylketene, also proposed by Chick and Wilsmore (14), fails adequately to account for the exclusive formation of γ -bromoacetoacetyl bromide (BrCH₂COCH₂COBr) by the addition of bromine, instead of the expected α -bromo compound, and for the formation of β -butyrolactone,

$$\begin{array}{c} \mathrm{CH}_3 & -\mathrm{CH} & -\mathrm{CH}_2 \\ | & | \\ \mathrm{O} & --\mathrm{CO} \end{array}$$

by hydrogenation. Formula III, β -crotonolactone, was recently postulated by Hurd (33) as a resonance isomer of acetylketene. Formula IV, vinylaceto- β -lactone, suggested by A. L. Wilson of this laboratory, with the exception of the formation of pyruvic aldehyde on ozonolysis (34), appears most satisfactorily to account for the reactions of diketene, including those involving halogenation and hydrogenation. In this paper the reactions of diketene to be described will be illustrated by the vinylaceto- β -lactone structure.

Physical Properties

Diketene is a colorless, nonhygroscopic liquid, insoluble in water but soluble in the common organic liquids inert toward it. It has an intensely pungent odor, and its vapors are extremely lachrymatory. Its physical properties are as follows:

Specific gravity, 20/20° C.	1.0897
Change in specific gravity, C.	0.0009
Molecular meight	9.09 (1099)
Boiling point, °C.	127.4
Melting point, ° C.	-6.5
Vapor pressure at 20° C., mm.	8.0
Latent heat of vaporization, calcd., cal./gram	165
Heat of combustion (2), cal./mole	447
Heat of formation, obsvd. (1), cal./mole	1081
Parachor $(M\gamma^{1/4})/D - d (34)$	181.5 (24.0° C.)
	183.2 (20.4° C.)
Refractive index, n ²⁰	1.4379

On standing at ordinary temperatures, it slowly polymerizes to a dark-colored, tarry material containing a substantial quantity of dehydroacetic acid, the dimer of diketene. The polymerization is greatly accelerated by mineral acids, alkali metal hydroxides, alkali metal alcoholates and phenolates, and tertiary aliphatic amines. As the reaction is exothermic, precautions must be taken to prevent these substances from coming in contact with large quantities of diketene. The tendency to polymerize is materially reduced by employing inert diluents, such as ethers, aromatic and aliphatic hydro-

carbons, esters, and ketones. Acetone has been found to be of particular value in this connection. Certain organic antioxidants, such as hydroquinone and pyrogallol, have a slight inhibiting action, but organic peroxides, such as benzoyl peroxide and ascaridole, do not appear to act as catalysts. Low temperatures retard the polymerization until it becomes negligible at the freezing point (-6.5°) C.). Samples of diketene have been stored in this laboratory under temperature conditions fluctuating between -30° and $+10^{\circ}$ C. for several years without any detectable change in physical or chemical properties. Of the common metals, aluminum has been found eminently satisfactory for storage and shipping containers. Accordingly, diketene may now be safely shipped and stored in a frozen condition in aluminum drums or other suitable containers. The availability of solid carbon dioxide affords an efficient and economical means of refrigeration. Diketene is best purified by distillation at subatmospheric pressure; the amount of polymerization occurring during distillation is a direct function of the temperature at which the distillation is carried out. Moreover, material distilled at a low temperature is more stable during storage than that distilled at a higher temperature.

In contrast to the majority of recently introduced aliphatic chemicals, whose chief values are their solvent powers or other specific properties, such as hygroscopicity, water miscibility, acidity, basicity, surface tension-depressing activity, and the like, the primary present and future industrial importance of diketene lies in its exceptional chemical reactivity and, consequently, in the products which may be synthesized from it. Because diketene is highly unsaturated, its most common reaction is the addition of substances having an active hydrogen atom to yield compounds containing the acetoacetyl group:

$$CH_2 = C - CH_2 + HA \longrightarrow CH_3COCH_2COA$$

Thus a large number of products derived from acetoacetic ester by the usual metathetical reactions may be synthesized more economically and with greater ease from diketene. For example, when acetoacetanilide and phenylmethylpyrazolone, two compounds of recognized commercial importance, are manufactured from diketene instead of acetoacetic ester, higher yields and purer products are obtained and the reaction time is substantially reduced. Moreover, the marked

The ketene dimer, diketene, is now available in commercial quantities. Because of its exceptional reactivity, its industrial importance lies in the valuable products which may be synthesized from it.

Diketene reacts with hydroxyl groups to form acetoacetic esters such as ethyl acetoacetate, with amino groups to form acetoacetamides such as acetoacetanilide, and with phenyl hydrazines to form phenylmethylpyrazolones. When reacted with ureas, diketene forms 4-methyluracils, and the reaction between diketene and aromatic hydrocarbons in the presence of aluminum chloride yields 1,3-diketones such as benzoylacetone. Halogens add to diketene to form γ -haloacetoacetyl halides, and β butyrolactone is formed when diketene is hydrogenated.

Diketene may be further polymerized by catalysts to yield a tetramer of ketene, dehydroacetic acid, which is noted for its varied chemical transformations.

By pyrolysis at $500-600^{\circ}$ C., diketene is depolymerized almost completely to ketene and thus affords a method for the rapid production of high-purity ketene. Ketene is a powerful acetylating agent; it reacts in general with compounds having an active hydrogen atom to give the corresponding acetyl derivative. exothermic nature of the reaction practically eliminates the necessity of externally applied heat. A summary of the more important reactions of diketene, together with a description of some of the products and their potential applications will be presented in the following pages (in several instances for the first time).

Reactions of Diketene

Diketene reacts with water in the presence of catalysts to give acetoacetic acid which, in turn, decomposes to acetone and carbon dioxide:

$$H_{2O} + \begin{array}{c} CH_2 = C - CH_2 \\ | & | \\ O - CO \end{array} \longrightarrow$$

CH₃COCH₂COOH

CH₃COCH₂COOH →

 $CH_3COCH_3 + CO_2$

With pure water the reaction is quite slow even at elevated temperatures, for a mixture of diketene and water in the absence of catalysts may be distilled at atmospheric pressure as a constant boiling mixture, over 90 per cent of the diketene remaining unchanged. The reaction between diketene and alcohols in the presence of acid catalysts yields the corresponding esters of acetoacetic acid (11):

$$\begin{array}{c} \operatorname{ROH} + \operatorname{CH}_2 = - - \operatorname{CH}_2 \longrightarrow \operatorname{CH}_3 \operatorname{COCH}_2 \operatorname{COOR} \\ | & | \\ O - \operatorname{CO} \end{array}$$

Thus, by this method ethyl acetoacetate can be produced in commercial quantities more easily and economically than by the classical sodium condensation of ethyl acetate. Also, the troublesome necessity of using sodium with its attendant hazards is eliminated. From both an academic and industrial standpoint, the importance of ethyl acetoacetate and its lower homolog, methyl acetoacetate, is too well known to require further comment. The number and variety of acetoacetic esters that may be synthesized from diketene appear to be limited only by the alcohols available, for the reaction is an extremely general one, applicable to all aliphatic alcohols from primary to tertiary, alcohol ethers, chlorohydrins, substituted alcohols, glycols, glycerol, and phenols. Acetoacetic esters similar to cellulose acetate have been reported as products of the reaction between diketene and cellulose (50).

Preparation of 2-Ethoxy Ethyl Acetoacetate

To 90 grams of 2-ethoxy ethanol ("Cellosolve") and 0.5 gram of benzene sulfonic acid at 100° C. were added dropwise, with agitation, 84 grams of diketene. Since an exothermic reaction occurred, the temperature was not allowed to rise above 110° C. When all the diketene had been added, the reaction mixture was kept at 100° C. for one hour, washed with water, and fractionally distilled under vacuum. An 84 per cent yield of ethoxy ethyl acetoacetate, CH₃COCH₂COO-C₂H₄OC₂H₅, was obtained as a colorless, water-insoluble, pleasant-smelling liquid which distilled at 93-94° C. at 3 mm.

Since the acetoacetic esters, in general, have the solvent power of both an ester and a ketone, they are useful as solvents for lacquers and other surface coatings, while those of higher molecular weight may be of value as plasticizers. Certain of their metallic salts have shown promise as resin stabilizers and oil-conditioning agents.

Diketene and primary aromatic mono- and polyamines react smoothly to yield the corresponding acetoacetyl amines in a high degree of purity and with excellent yields (10). Representative of this type of compound is acetoacetanilide, prepared from diketene and aniline (40):

$$CH_{2} = C - CH_{2} + NH_{2}C_{6}H_{5} \longrightarrow CH_{3}COCH_{2}CONHC_{6}H_{5}$$

The acetoacetanilides are used as intermediates for the production of the Hansa yellow dyes, formed by coupling them with diazonium compounds (30). Because of their stability, light fastness, insolubility in the common organic solvents, and great tinctorial value, the Hansa yellows are becoming increasingly important as pigments for a wide variety of surface coatings.

Diacetoacetyl diamino compounds of the diaryl series are extensively used as developers for producing azo dyes directly on cotton (39). In this process an alkaline solution of the acetoacetyl amine is padded onto the fiber, then developed with a diazonium compound. Typical compounds of this series are N,N'-diacetoacetylbenzidine, CH₃COCH₂CONHC₆H₄— C₆H₄—NHCOCH₂COCH₃, and N,N'-diacetoacetyl-o-tolidine, CH₃COCH₂CONHC₆H₃(CH₃).C₆H₃(CH₃)NHCOCH₂COCH₃, commonly known as "Naphthol ASG", prepared by reacting two moles of diketene with one mole of benzidine and o-tolidine, respectively.

Diacetoacetyl-o-Tolidine

To a refluxing solution of 212 grams of *o*-tolidine in 1700 cc. of ethylene dichloride were added slowly, with agitation, 184 grams of diketene over a period of one hour. During this time the reaction was sufficiently exothermic to keep the solution refluxing without the application of external heat. When the diketene had all been added, the mixture was allowed to stand at room temperature for 16 hours and was then filtered. There were obtained 354 grams of pure diaceto-acetyl-o-tolidine, melting at 206-207° C. and representing a yield of 93 per cent.

When treated with strong dehydrating agents such as sulfuric or phosphoric acid, acetoacetanilides undergo ring closure to form 4-methylcarbostyril and its derivatives. Thus, the simplest of these compounds, 4-methylcarbostyril itself, is obtained in practically quantitative yields by dissolving acetoacetanilide in concentrated sulfuric acid (37), followed by precipitation with water:



When dehydrated, substituted acetoacetanilides yield the correspondingly substituted 4-methylcarbostyrils. These compounds have shown activity as corrosion inhibitors and bactericides; their use as intermediates for dyestuffs and pharmaceuticals is also indicated.

Although in most cases the reaction between diketene and aromatic amines is most efficiently carried out in inert organic solvents as reaction media, the great difference in reactivity of diketene with water and primary amine groups makes it possible to run these reactions in water, the amine being either in solution or suspension (9). Diacetoacetylbenzidine can be prepared by adding diketene to an agitated suspension of finely divided benzidine in water; N,N'-diacetoacetyl-*p*-phenylene diamine is readily formed by introducing diketene into an aqueous solution of *p*-phenylene diamine.

Similarly, diketene reacts with aqueous solutions of ammonia and primary and secondary aliphatic amines, the products being acetoacetamide or nitrogen-substituted aceto-acetamides (9):

$$\begin{array}{c} \mathrm{CH}_{2} = \mathrm{C-CH}_{2} \\ \downarrow \\ \mathrm{O-CO} \end{array} + \mathrm{NH} \Big\langle \begin{array}{c} \mathrm{R}_{1} \\ \mathrm{R}_{2} \end{array} \to \mathrm{CH}_{3} \mathrm{COCH}_{2} \mathrm{CON} \Big\langle \begin{array}{c} \mathrm{R}_{1} \\ \mathrm{R}_{2} \end{array} \right\rangle$$

where R_1 and $R_2 = H$ or alkyl groups

Here is presented a method for preparing acetoacetyl primary and secondary aliphatic amines which have not previously been described in the literature. As examples of such products might be mentioned acetoacetamide, N,N'-diacetoacetylethylene diamine, and N-acetoacetylmorpholine, obtained by reacting diketene with aqueous solutions of ammonia, ethylene diamine, and morpholine, respectively.

Diacetoacetylethylene Diamine

To a solution of 30 grams (one-half mole) of ethylene diamine in 500 cc. of water at 0° C. were added dropwise, with stirring, 84 grams (one mole) of diketene over a period of an hour; the temperature was kept below 20° C. During the reaction the product started to crystallize from solution. When all the diketene had been added, the mixture was stirred for one hour and filtered, and the product washed with water. A 72.4 per cent yield of N,N'-diacetoacetylethylene diamine, CH₃COCH₂CONH—C₂H₄—NHCOCH₂COCH₃, was obtained as a colorless, crystalline solid which melted at 168–169° C. with diazonium compounds (19). Phenylmethylpyrazolone also serves as the starting material in the synthesis of the valuable analgesic, "Antipyrine" (38). In connection with the manufacture of pyrazolones, the strong tendency of diketene to react with amino groups, even in the presence of



UNIT FOR THE REACTION OF DIKETENE WITH AN ABYL AMINE

The aliphatic acetoacetamides are colorless, crystalline solids similar in chemical properties to acetoacetanilide and acetoacetic ester. They form metallic salts. They may be alkylated and acylated by the usual methods, and the nitrogen-substituted compounds form dyes when coupled with diazonium compounds. The lower members of the series have indicated value as dye solvents, constituents of wood stains, and as intermediates for the preparation of formaldehyde condensation resins. When heated, acetoacetamide condenses with itself to form lutidone carboxylic acid and lutidone, compounds of interest as intermediates for further syntheses (18).

When diketene is reacted with urea or symmetrical disubstituted ureas in an inert solvent, 4-methyluracil or its homologs are formed (8). The reaction involves the intermediate formation of an *N*-acetoacetylurea, which then undergoes ring closure through elimination of water to yield the uracil:



At temperatures around room temperature, diketene reacts with phenylhydrazine in an inert solvent to form the phenylhydrazone of acetoacetylphenylhydrazine, $CH_sC(==N--N-HC_6H_5)CH_2CONHNHC_6H_5$ (15). If, however, higher temperatures are employed, the reaction takes a different course, yielding 1-phenyl-3-methyl-5-pyrazolone in high efficiency (36). Phenylmethylpyrazolone, known to the dyestuff trade as "Developer Z", and its derivatives are constituents of an important class of azo dyes formed by coupling water, makes it possible to prepare sulfophenylmethylpyrazolone, also a well known dye intermediate (20), by this method. The starting material, phenylhydrazine sulfonic acid, is practically insoluble in inert organic solvents; consequently no reaction takes place with diketene under such conditions. But when diketene is added to an aqueous suspension of phenylhydrazine sulfonic acid, smooth reaction takes place and good yields of 1-sulfophenyl-3-methyl-5pyrazolone result:



1-Sulfophenyl-3-Methyl-5-Pyrazolone

To a stirred suspension of 315 grams of an aqueous paste, containing 31.7 per cent of phenylhydrazine sulfonic acid in 1500 cc. of water maintained at 0–10° C., 50 grams of diketene were added dropwise, over a period of 45 minutes. Stirring was continued for 4 hours; then the reaction mixture was evaporated on a water bath to a thick paste, in which form the product is most suitable for commercial use. Analysis of the paste by titration with 0.5 N benzene diazonium chloride solution showed that it contained 112 grams of 1-sulfophenyl-3-methyl-5-pyrazolone, representing a yield of 80 per cent.

Ketones, esters, and ethers apparently do not react with diketene. With aldehydes higher than formaldehyde, an aldol-type condensation takes place, the final products being alpha-beta-unsaturated ketones (7). In this reaction an intermediate hydroxy diketene is believed to be formed, which subsequently loses water. The water eliminated reacts with the condensation product and results in the formation of a β -ketocarboxylic acid, which, in turn, loses carbon dioxide; the end product is the unsaturated ketone:

In practice the reaction is carried out by refluxing diketene and the aldehyde in molar ratio, with or without a solvent for 24-48 hours, and then separating the product by fractional distillation. When heated, formaldehyde and diketene react to form a polymeric resinous material (6).

When hydrogenated in the liquid phase in the presence of Raney nickel, diketene yields β -butyrolactone in high efficiency and, in addition, a small amount of butyric acid (35, 43):

$$\begin{array}{c} CH_2 = C - CH_2 + H_2 & \xrightarrow{Ni} & CH_3CH - CH_2 \\ \downarrow & \downarrow & \downarrow \\ O - CO & & O - CO \end{array}$$

 β -Butyrolactone may be readily hydrolyzed to β -hydroxybutyric acid, a compound of pharmaceutical importance and an intermediate for the preparation of a great number of esters and acyl derivatives useful as solvents and plasticizers. Chloroacetoacetyl chloride is stable only at low temperatures and cannot be purified by distillation. It reacts as an acid chloride and is of value for synthesizing compounds containing the chloroacetoacetyl group, such as γ -chloroacthyl acetoacetate, ClCH₂COCH₂COOC₂H₅, and γ -chloroacetoacetanilide, ClCH₂COCH₂CONHC₆H₅. Since, in addition to an active methylene group, these compounds contain an amide or ester linkage, their use as synthetic intermediates is suggested. When reacted with water, γ -chloroacetoacetyl chloride hydrolyzes to monochloroacetone, carbon dioxide, and hydrochloric acid:

 $ClCH_2COCH_2COCl + H_2O \longrightarrow ClCH_2COCH_3 + CO_2 + HCl$

The chloroacetone obtained in this manner is free of higher chlorinated acetones; hence the chlorination and subsequent hydrolysis of diketene offer a convenient method for preparing this material in a pure state. Starting with γ -bromo-acetoacetyl bromide, pure monobromoacetone is obtained in like manner.

Another series of derivatives of diketene of considerable interest are the aromatic 1,3-diketones typified by benzoylacetone, $CH_3COCH_2COC_6H_5$, which can be economically prepared by reacting diketene with aromatic hydrocarbons in the presence of aluminum chloride. Diketene appears to function in this reaction as do acid anhydrides in the Friedel-Crafts synthesis, the maximum yields being obtained when two moles of aluminum chloride are employed with one mole of diketene:

$$CH_2 = C - CH_2 + C_6H_6 \xrightarrow{\text{2AlCl}_3} CH_3COCH_2COC_6H_6$$



A MODERN SYNTHETIC ORGANIC CHEMICAL PLANT

Diketene, either in the pure state or dissolved in an inert solvent, rapidly absorbs chlorine at low temperatures to yield γ -chloroacetoacetyl chloride, a reaction readily accounted for by the vinylaceto- β -lactone structure:

$$\begin{array}{c} \mathrm{CH}_2 = \mathrm{C-CH}_2 \\ | & | \\ \mathrm{O-CO} \end{array} + \mathrm{Cl}_2 \longrightarrow \mathrm{ClCH}_2 \mathrm{COCH}_2 \mathrm{COCI} \end{array}$$

Similarly, bromine adds to diketene to form γ -bromoacetoacetyl bromide (15). An addition compound of aluminum chloride and diketene is probably first formed as an intermediate, which then adds to the hydrocarbon under the activating influence of a second mole of aluminum chloride.

Benzoylacetone

A 2-liter three-neck flask, fitted with a reflux condenser, mercury-sealed stirrer, and dropping funnel, was charged with 532 grams (four moles) of anhydrous aluminum chloride and 1100 cc. of benzene. Over a period of 90 minutes 168 grams (two moles) of diketene were added dropwise with stirring, while the temperature was kept between 45° and 50° C. A vigorous exothermic reaction took place, accompanied by a copious evolution of hydrogen chloride. When all the diketene had been added, the reaction mixture was heated, with stirring, at 65-75° C. for 2 hours, and was then cooled and decomposed by pouring onto 1500 grams of chopped ice. After excess benzene was removed by steam distillation, 250 cc. of concentrated hydrochloric acid were added and the mixture was refluxed for 2 hours. On cooling, benzoyl acetone separated in an impure form as a brown, crystalline solid, which was separated on a filter, washed with cold water, dried, and purified by fractional distillation under reduced pressure. There were obtained 237 grams of benzoylacetone as a colorless solid which distilled at 140-141° C. at 15 mm. and melted at 58-59°C. The yield was 73 per cent, based on the diketene used.

The aromatic 1,3-diketones are colorless, crystalline solids or pale yellow, high-boiling liquids soluble in alcohols, ethers, esters, ketones, chlorinated solvents, and aromatic hydrocarbons, sparingly soluble in water, but completely soluble in dilute alkali solutions. The presence in the molecule of an aromatic nucleus combined with two ketone groups confers unique solvent properties, which make them of interest as plasticizers, particularly for resins of the vinyl type. Chemically they exhibit all the typical reactions of 1,3-diketones. They may be alkylated or acylated at the methylene carbon atom by the usual methods, they form extremely stable chelated compounds with polyvalent metals (12) which show promise as resin stabilizers and oil-conditioning agents, and they are converted into dyes when coupled in alkaline solution with diazonium compounds (31). Primary aromatic amines condense with benzoylacetone to give imino derivatives which, on dehydration, yield quinaldines (5); the latter are of interest in the photographic field. Also, when reacted with hydroxylamines and hydrazines, isoxazoles (17) and pyrazoles (27), respectively, are formed.

Dehydroacetic Acid

As has been pointed out, one of the characteristic properties of diketene is its tendency to polymerize to higher ketene polymers. Slow polymerization or polymerization induced by a catalyst and then allowed to proceed uncontrolled, results in the formation of dark-colored, tarry products from which only a small amount of dehydroacetic acid can be isolated with difficulty. In order to obtain dehydroacetic acid economically from diketene, it is essential to carry out the polymerization under controlled conditions which will minimize the formation of higher polymers. This treatment is best accomplished by adding diketene slowly to an inert solvent at 70-120° C., containing a small amount of catalyst. As catalysts, tertiary amines, such as pyridine, triethylamine, and methylmorpholine, and alkali metal salts of hydroxyl compounds, such as sodium ethylate and sodium butylate. have been found most efficient; aromatic hydrocarbons, such as benzene and toluene, are most suitable as solvents. When polymerized under these conditions, diketene, yields from 60 to 80 per cent of dehydroacetic acid:



Dehydroacetic acid is a colorless, crystalline compound melting at 109° and boiling at 274° C.; from a chemical standpoint it is noteworthy for the large number of derivatives into which it may be transformed by the action of acids and alkalies under varying conditions. Among them might be mentioned the formation of triacetic lactone (22), acetylacetone (22), and isodehydroacetic acid (24) by the action of strong sulfuric acid, and of diacetylacetone (25) and dimethylpyrone (3) which result from the hydrolysis of dehydroacetic acid with concentrated hydrochloric acid. Diacetylacetone and dimethylpyrone, in turn, react with ammonia and primary amines to yield a series of lutidone derivatives which deserve investigation in the pharmaceutical and dyestuffs fields. Orcinol, a dihydric phenol which has interesting possibilities as a photographic developer and antioxidant, and malonic acid are reported as products resulting from the action of concentrated alkali on dehydroacetic acid (23, 45).

Ketene

Just as diketene may be converted largely to its dimer, dehydroacetic acid, by polymerization under the proper conditions, conversely it may be depolymerized quantitatively to its monomer ketene by pyrolysis; thus for the first time a convenient and simple process for rapidly producing pure ketene uncontaminated by methane and other hydrocarbons and oxides of carbon is available:

$$\begin{array}{c} CH_2 = C - CH_2 \\ | & | \\ O - CO \end{array} \longrightarrow 2CH_2 = CO$$

The pyrolysis may be carried out efficiently either by refluxing diketene over metal filaments, such as platinum or other resistant metal, heated to a dull redness, or by passing the vapor through a tube heated to 550-600° C. For the laboratory preparation of ketene, a modification of the Ott ketene lamp (42) was found most satisfactory. This device consists of a 200-cc. flask surmounted by a pyrolysis chamber of glass, 18 cm. long and 5 cm. in diameter, in which is suspended a filament of 70 cm. of No. 30 B. and S. gage platinum wire; the glass frame on which the wire is mounted is sealed to a ground-glass stopper so that the filament can be removed easily. The pyrolysis chamber is fitted at the top with a reflux condenser leading to a flask immersed in an ice bath to collect unchanged diketene entrained by the ketene vapors. From this flask the ketene is led into and condensed in a cold trap cooled by a solid carbon dioxide-acetone bath. The data from a typical run, where 100 grams of diketene were refluxed for 25 minutes over platinum filament heated to a dull redness by a current of 5 amperes, are as follows:

Residue, grams	5.6
Unchanged diketene condensed in first ice-cooled trap, grams	38.5
Ketene condensed, grams	55.5
Material accounted for, grams	99.6
Ketene from pyrolyzed diketene, %	99.1
Rate of ketene production:	
Grams per minute	2.2
Moles per hour	3.17

On a larger scale ketene is produced with equal efficiency by passing the vapors of diketene through a tube heated to 550-600° C., liquid diketene being first vaporized by flash evaporation or other convenient means.

Ketene is a colorless, highly toxic gas boiling at -56° and melting at -134.6° C. (44). When inhaled in low concentration, it leaves a peculiarly disagreeable taste in the mouth and slight irritation in the lungs and nasal passages which persists for several hours or longer after exposure. Curiously this effect is greatly heightened by smoking or by the mere presence of tobacco smoke in the atmosphere. The tendency of ketene to polymerize is even more marked than that of diketene; hence it cannot be stored or shipped in the gaseous state or in solution but must be reacted immediately after preparation.

Ketene, which is the internal anhydride of acetic acid, is a powerful acetylating agent; it reacts, in general, with compounds having an active hydrogen atom to give an acetyl derivative:

$$CH_2 = C = O + HA \longrightarrow CH_3COA$$

Aliphatic alcohols from primary to tertiary react with ketene to give the corresponding acetic acid esters. Ketene has also been used as an acetylating agent for polyhydroxy compounds, such as glycols and glycerols (29), vegetable oils (28), resins of the glyptal type (13), and cellulosic materials (41). Phenyl acetate (47) and acetylsalicylic acid (aspirin) (1) have been prepared in almost quantitative yields by reacting ketene with phenol and salicylic acid, respectively. Thioacetates are obtained from ketene and thioalcohols (32).

Ketene reacts with gaseous or aqueous ammonia to give acetamide and with primary and secondary aliphatic amines to yield nitrogen-substituted acetamides. For example, from monoethanolamine and aniline, respectively, N-hydroxyethylacetamide and acetanilide are formed. N-chloroacetamide, CH₃CONCIH, results from the addition of chloramine, NH_2Cl , to ketene (21).

Ketene reacts preferentially with amino groups in the presence of water and has been reported as a valuable means for acetylating amino acids in aqueous solution (4). Ketene has also been found to be an effective agent for the detoxification of vaccines (49).

Organic acids react with ketene to yield mixed anhydrides which, on distillation, break down to acetic anhydride and the anhydride of the acid (46). Chloroacetyl chloride is easily prepared by the addition of chlorine to ketene, either in the vapor phase or in solution:

$CH_2 = C = 0 + Cl_2 \longrightarrow ClCH_2COCl$

Chloroacetyl chloride is a useful intermediate for the preparation of a number of commercially important products, such as chloroacetic acid, the hydrolysis product of chloroacetyl chloride, chloroacetamide, prepared by reacting chloroacetyl chloride with ammonia, and chloroacetophenone, the important vesicant which is obtained by reacting chloroacetyl chloride with benzene in the presence of aluminum chloride. Anhydrous hydrogen chloride adds to ketene to produce acetyl chloride (26). Liquid hydrogen sulfide and ketene form thioacetic anhydride, (CH₃CO)₂S (16); malonyl chloride, CH₂(COCl)₂, which can be hydrolyzed to malonic acid, may be obtained from ketene and phosgene.

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